DEACTIVATION BY CARBON OF NICKEL AND NICKEL-MOLYBDENUM METHANATION CATALYSTS

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INTRODUCTION

A serious problem in the catalytic methanation of coal synthesis gas is fouling of the catalyst by carbon deposition. This problem can be avoided by increasing the hydrogen content of the feed stream so that thermodynamic equilibrium is unfavorable toward carbon deposition (1); however, process economics favor minimizing hydrogen usage. Since most gasifiers produce a hydrogen deficient gas the application of a methanation catalyst which deposits carbon at negligible rates would be highly desirable, since it would eliminate the need for the shift reactor prior to methanation. Except for a few recent studies in this laboratory (2-5) there has been very little research to determine the effects of carbon deposition on activity or the kinetics and mechanism of carbon deposition on various catalysts during methanation. Such information would be valuable in determining the best catalysts and optimum operating conditions for methanation of hydrogen-poor synthesis gas.

A previous study in this laboratory (6) showed that Ni-Mo catalysts are promising for use in the BI-GAS process since they are as active as Ni but more resistant to sulfur poisoning. The present study was undertaken to determine the behavior of Ni and Ni-Mo catalysts under reaction conditions which are characteristic of combined shift/methanation and which favor massive carbon formation. The objectives of this study were to:

1. Determine the effects of carbon deposition on the activity of these catalysts under high temperature conditions (both low and high pressures) which promote carbon formation.

2. Determine if the carbon fouled catalysts could be regenerated by treatment in air or O_2 at high temperatures.

The results of activity, adsorption, carbon deposition and regeneration tests to accomplish these objectives are presented and discussed in this paper.

EXPERIMENTAL METHODS

Materials

Catalyst composition and suppliers are listed in Table 1. Catalyst preparation and pretreatment was the same as described previously (6).

Hydrogen gas (99.99% Whitmore) was purified using a Pd catalyst followed by a molecular sieve trap. Gases for the reaction mixtures, N_2 (99.99% Whitmore), CO (99.99% Matheson) CH_4 (99.97% Matheson), CO_2 (99.8% Whitmore) were used as delivered. The reaction mixture for the carbon deposition runs was passed through an activated charcoal trap heated to 473 K and a ZnO/molecular sieve trap heated to 353 K to remove any iron carbonyl and sulfur impurities before undergoing methanation. Catalyst presulfiding treatments were carried out using a 66 ppm H_2S in H_2 mixture prepared in this laboratory diluted to 9 ppm with hydrogen.

Procedure

H_2 Chemisorption. Prior to each test series, small samples (0.2-0.5 g) of reduced catalysts were rereduced at 773 K as previously described (6). H_2 adsorption isotherms were then measured at 298 K following procedures reported previously (7-9). H_2 chemisorption measurements were also performed following each series of tests to detect any changes in the catalyst surface area, and in the case of catalysts analyzed for carbon content H_2 chemisorption measurements were made directly after carbon deposition.

Specific Rate Measurement. Except for the fluidized bed tests specific rates were measured in a Pyrex, fixed-bed reactor at 498 K before and after the steady state carbon deposition runs and after regeneration in the same manner as in our previous study (6). Specific rate measurements for catalysts deactivated in the fluidized bed reactor were performed only after regeneration. Except for the measurements before and after high pressure carbon deposition these tests were performed with 0.2 to 0.6 gram samples and a reactant mixture consisting of 1% CO, 4% H_2 and 95% N_2. To avoid lengthy reduction and passivation steps, the specific rate measurements before and after the high pressure carbon deposition runs were carried out in the stainless steel high pressure reactor described previously (6) using 1 ml samples. The reactant mixture for these measurements was 4.3% CO, 5.6% H_2 and 90.1% N_2.

Steady State (24 h) Carbon Deposition Runs. After initial specific rate measurements, each catalyst was operated in a fixed bed for approximately 24 hours under steady state conditions at 723 K and pressures of 138 kPa or 2600 kPa to observe its behavior under severe carbon deposition conditions. Two samples of each catalyst were run at the lower pressure. One was used for regeneration tests and one was analyzed for carbon content. The space velocity for all steady state carbon deposition runs was 100,000 h^{-1}. Operation in the carbon deposition region of the equilibrium diagram was ensured by using a 4.2% CO mixture (in a N_2 diluent) and a H_2/CO ratio of 1.3. Figure 1 shows this composition on a carbon-hydrogen-oxygen triaxial plot along with our 1% CO mixture (H_2/CO = 4) and the BI-GAS nominal feed gas composition (H_2/CO = 1.4). Sample sizes were again 0.2-0.6 g for low pressure runs and 1 ml for high pressure runs. Reactant and product sampling was performed in the same way as in our previous in situ deactivation measurements (6).

Ni-Mo-Cu (0.57 g) and Ni-Mo (0.51 g) were operated in a fluidized bed reactor (6) for 24 hours at 723 K and 138 kPa. A fluidized bed was used in order to simulate more closely the BI-GAS process. The reaction mixture was a dilute BCR mixture of the following composition: 5.3% CO, 6.5% H_2, 1.6% CH_4, 3.6% CO_2, 83.0% N_2. These runs were repeated using fresh samples (0.5-0.6 g) and a 4.2% CO, 5.5% H_2, 90.3% N_2 mixture to obtain samples for carbon analysis.

Regeneration Tests and Passivation. Regeneration tests were performed with a 1-3% air in N_2 mixture at 138 kPa for catalysts deactivated at low pressure and a 1-4% O_2 in N_2 mixture at 2600 kPa for those deactivated at high pressure. In both cases the temperature was 573 K. Catalysts deactivated in a fluidized bed were also regenerated in a fluidized bed. During regeneration CO and CO_2 concentrations in the product stream were monitored continuously with the chromatograph for 15 to 30 minutes. After 30 minutes the CO_2 concentration was negligible indicating completion of carbon removal. The catalysts which had undergone either high pressure regeneration or low pressure fluidized bed regeneration were passivated with a dilute air/N_2 mixture and transferred to the fixed bed reactor cell to facilitate subsequent specific rate and H_2 chemisorption measurements.

Regeneration of the Ni catalyst was attempted using a 50% H_2O/H_2 mixture at 723 K and 2600 kPa for 6.5 hours, but it resulted in severe attrition and there was not enough catalyst left in the reactor to perform any meaningful tests. For this reason a dilute O_2/N_2 mixture at high pressure was used for regeneration of catalysts deactivated at high pressure.

Pre-sulfiding Runs. 0.5 ml samples of the Ni and Ni-Mo-Cu catalysts were loaded into the Pyrex fluidized bed reactor and re-reduced as discussed previously. The fluidized bed was used to assure uniform poisoning of the catalyst particles. These catalysts were then exposed to 375 ml/min of a gas mixture of 9 ppm H_2S in H_2 at 725 K for sufficient time to sulfide 50% of the catalyst surface (6). After exposure for the required time, the catalysts were cooled to room temperature and passivated. Activity tests were then run as described below.

RESULTS

Specific Rate and H_2 Chemisorption Measurements

Reaction rates per active site of catalyst, i.e. methane turnover numbers (N_{CH_4}), and product yields (fractions of converted CO occurring as various products) obtained in differential reactor tests of Ni, Ni-Mo, and Ni-Mo-Cu catalysts are presented in Table 2 along with H_2 chemisorptive uptakes.

The data in Table 2 show that all three catalysts suffered significant decreases in metal surface area measured by H_2 adsorption after carbon deposition at either low or high pressure. However, there were significant variations in the magnitude of changes observed for turnover numbers after carbon deposition at low pressure. The CH_4 turnover numbers of Ni and Ni-Mo-Cu did not change significantly while that of Ni-Mo dropped over 90%. CH_4 yield dropped for Ni and Ni-Mo but remained unchanged for Ni-Mo-Cu. Ni-Mo-Cu and Ni-Mo exhibited significant increases in CO_2 yield after carbon deposition, whereas Ni showed no significant CO_2 yield either before or after carbon deposition.

The catalysts also responded differently to regeneration. Ni and Ni-Mo regained activity after regeneration having CH_4 turnover numbers near those for the fresh catalysts; CH_4 yield was almost completely restored for Ni but only in part for Ni-Mo. Regeneration did not improve the activity or selectivity of Ni-Mo-Cu, but rather caused decreases in CH_4 and CO_2 yields. All of the sulfur-free catalysts apparently suffered a decrease in surface area after regeneration.

The results of differential runs for catalysts subjected to carbon deposition at high pressure demonstrated similar trends. That is, CH_4 turnover numbers as well as CH_4 yields decreased for all catalysts. In fact N_{CH_4} decreased by a factor of 2 for Ni and a factor of 10 for Ni-Mo-Cu and Ni-Mo.

Despite a decrease in surface area the regeneration treatment at high pressure with a dilute O_2 mixture seemed to greatly improve catalyst performance for all catalysts. CH_4 turnover numbers for the three catalysts ranged from 1.5 to 8 times the value before carbon deposition and CH_4 yields were 37 to 66 percent higher than pre-carbon deposition values. To determine if this effect was permanent the Ni catalyst was tested for an additional 20 hours at 623 K and space velocity of 100,000 h^{-1} with 1% CO and $H_2/CO = 4$, after which the turnover number reverted to the pre-carbon deposition value.

Table 2 also shows the results of differential tests on two catalysts, Ni-Mo-Cu and Ni, which were pre-sulfided and exposed to carbon depositing environment at low pressure. These results show that carbon deposition is extremely detrimental to Ni-Mo-Cu when it has been previously exposed to H_2S. On the other hand Ni is

relatively unaffected showing similar activity performance to the non-sulfided catalyst. Both catalysts showed little change in H_2 uptake as a result of carbon deposition and/or regeneration. However, regeneration apparently caused a significant increase in CH_4 yield for pre-sulfided Ni.

Steady State (24 h) Carbon Deposition Tests

Values of CO conversion, rates of methane production and normalized activities are listed in Table 3 for Ni, Ni-Mo and Ni-Mo-Cu catalysts before and after 24 hour steady state tests at 773 K and 100,000 h^{-1}. Typical plots of normalized activity versus time are shown in Figures 2 and 3. Normalized activity is defined as the ratio of the instantaneous rate of methane production to the initial rate; the half life corresponds to a normalized activity of 0.5.

Based on the normalized activity after 24 hours the order of decreasing resistance to carbon deposition at low pressure was Ni, Ni (pre-sulfided), Ni-Mo-Cu, Ni-Mo, Ni-Mo-Cu (pre-sulfided). The order of increasing content of carbon deposited after 24 hours followed this same trend. However, when the Ni-Mo and Ni-Mo-Cu catalysts were operated in a fluidized bed, Ni-Mo maintained an activity of 0.38 compared to zero for Ni-Mo-Cu after the 24 hour carbon deposition test, even though 10 times more carbon was deposited on Ni-Mo compared to Ni-Mo-Cu. In fact, the Ni-Mo-Cu catalyst lost all measurable activity within 15 hours in the fluidized bed. The pre-sulfided Ni-Mo-Cu also deactivated very rapidly as shown in Figure 2. Figure 3 shows fairly significant fluctuations in the data at 8 hours for the Ni-Mo fluidized bed run. Maintenance of a steady flow during this run required constant attention, and this fluctuation can be attributed to flow variations during the evening and night hours when the run was unattended.

Data in Table 3 obtained at high pressure show that Ni-Mo lost no activity during the 24 hour period. Only a slight decrease in activity was observed for Ni, whereas the activity for Ni-Mo-Cu decreased by almost 40%.

For the low pressure fixed bed carbon deposition runs the decrease in normalized activity with time is represented best by the following expression:

$$a = \frac{a_o}{1+\exp(-ka_o\tau)[\exp(k_d[CO^o]t)-1]} \qquad 1)$$

where a = normalized activity at time t, a_o = normalized activity at t = 0, k = reaction rate constant (h^{-1}), k_d = decay constant ($1 \ mol^{-1} \ h^{-1}$), t = time (h), $[CO^o]$ = concentration of CO at bed entrance ($mol \ l^{-1}$), and τ = inverse space velocity (h). An expression for the half life ($t_{1/2}$) is obtained from Equation 1 by setting a/a_o = 0.5 and rearranging. The result is

$$t_{1/2} = \frac{1}{k_d[CO^o]} \ln [\exp (ka_o\tau) + 1] \qquad 2)$$

Equations 1 and 2 were used to plot the solid lines in Figures 2 and 3 and to calculate the half lives shown in Table 3.

The data from the fluidized bed runs are correlated fairly well by the following expression after about 5 hours:

$$a = a_o e^{-k_d t} \qquad 3)$$

where the symbols have the same meaning as before. From Equation 3 the half life can be obtained as follows:

$$t_{1/2} = 0.693 \ (k_d)^{-1} \hspace{3cm} 4)$$

This expression was used to calculate the half lives of Ni-Mo and Ni-Mo-Cu in a fluidized bed which are shown in Table 3.

DISCUSSION

Effects of Carbon Deposition on Methanation Activity

Effects on Intrinsic Activity/Selectivity Properties. Several recent investigations of methanation over Ni, and Ru catalysts (10-12) have provided evidence that adsorbed carbon is an active reaction intermediate. McCarty and Wise (11) reported four types of carbon which are adsorbed on the Ni surface after exposure to CO. Two species designated α'-carbon and α-carbon (both atomic carbon) were easily removed by H_2 and another designated β-carbon (polymerized carbon) was about 1/100 as active toward H_2. Graphitic carbon, the fourth type is apparently formed by high temperature conversion of the β-form. McCarty and Wise indicated that α-carbon (C_α) is slowly transformed to β-carbon (C_β) at temperatures above 600 K. Thus, carbon fouling of methanation catalysts is likely the result of C_β formation from C_α, the rate of transformation probably depending on the nature of the active site. The more active sites are more likely to promote both rapid deposition and gasification of C_α. If deposition occurs more rapidly than gasification, C_α will build up on the surface and C_β formation will be favored.

Assuming carbon is an active intermediate, the deactivation rate is then determined by the relative contributions of the rate of active carbon formation and the rate of gasification. The relationship between rates of carbon formation and gasification forms the basis of the following discussion of individual catalyst behavior under low pressure conditions. Apparently under the low pressure conditions of this study Ni shows very little deactivation and accumulates very little carbon. This behavior suggests that the rate of gasification equalizes the rate of deposition for nickel under these conditions. The small amount of carbon fouling that did occur appears to be mainly due to blockage or loss of sites since carbon deposition did not change the turnover number. The addition of Mo to Ni apparently favors the massive deposition of carbon as evidenced by the very significant loss of specific activity and greater carbon content of Ni-Mo. Indeed, recently obtained data from a gravimetric study in this laboratory (4,5) show that the rate of carbon deposition at 773 K on a 5.5% Ni-Mo/Al_2O_3 catalyst is 5 times greater than for a 3% Ni/Al_2O_3 catalyst. The major difference in behavior of these two catalysts appears to be the significantly higher rate of gasification of carbon for the 3% Ni/Al_2O_3. Perhaps Mo believed to be present as MoO_2 dissociates CO but not H_2, thus catalyzing formation but not removal of C_α.

The addition of Cu to Ni-Mo appears to cause a reduction in the amount of C_α formed as indicated by the significantly lower turnover number of Ni-Cu-Mo. Consequently little C_β is formed, resulting in the relatively long half-life of Ni-Mo-Cu relative to Ni-Mo. Ponec (10,12) suggests that in order to dissociate adsorbed CO and form the active surface carbon species an ensemble of active Ni sites is necessary, and that addition of Cu, itself inactive towards methanation, dilutes the active Ni sites causing lower methanation activity of Ni-Cu catalysts as compared to Ni catalysts.

The change in selectivity observed for all catalysts after low pressure carbon deposition suggests some type of modification of the active sites. It is also reasonable to expect that a carbon covered surface will behave catalytically more like a metal carbide than a clean metal surface. This is supported by previous work of McCarty et al. (13,14) and Sexton et al. (15). In addition, massive deposits of carbon in filamentous form have been shown by previous workers to separate and encapsulate metal crystallites. Thus formation of large amounts of C_β may place the metal crystallites in a new support environment, the subsequent change in metal-support interactions inducing changes in activity/selectivity properties. In the case of bimetallic catalysts metal-carbon interactions may induce changes in surface composition which affect selectivity. Ponec (12), for example, presents evidence for the surface modification of a Ni-Cu film by repeated adsorption and temperature programmed desorption of CO.

The data in Table 2 suggest that carbon deposition at high pressure may increase the amount of C_β formed in the case of Ni and Ni-Mo catalysts. That is, the percentage decrease in CH_4 turnover number observed after high pressure carbon deposition is equal to or greater than that observed in the low pressure runs. This observation can be explained on the basis of CO partial pressure. At high pressure the minimum partial pressure of CO was 10 kPa (assuming 90% conversion) whereas the maximum partial pressure of CO in the low pressure carbon deposition tests was 6 kPa. At a higher partial pressure of CO the adsorption and dissociation of CO on the catalyst surface proceeds at a much greater rate (4,5). If the carbon formation rate is greater than the gasification rate more C_β will result.

Effects of Carbon Deactivation on Apparent Activity/Selectivity Properties in a Fixed Bed at High Temperature, Conversion Conditions. Even though considerable carbon fouling was evident, relatively little deactivation was observed during steady state deposition tests for most catalysts except Ni-Mo-Cu (see Figs. 2 and 3). This was particularly true at high pressure. This behavior indicates that only a portion of the active sites are necessary to maintain a high reaction rate. It is therefore reasonable to assume that in a fixed bed reactor most of the reaction takes place in a small zone at the entrance to the bed, creating a large concentration gradient over the reactor. In this small zone, the CO partial pressure is large and the rate of formation of C_β is high; further downstream the catalyst is subjected to a lower CO partial pressure and less C_β is formed. Thus a reaction zone is created which gradually moves downstream as the catalyst becomes fouled. Therefore, at high temperature, high conversion conditions and especially at high pressure, we would expect to observe very little deactivation until the reaction zone reaches the end of the bed. The catalyst would then exhibit an extremely rapid deactivation similar to the depletion of an ion-exchange column. Thus, the true deactivation behavior in a fixed bed at high temperatures and especially at high pressures is masked by heat and mass transfer limitations.

Ni-Mo-Cu exhibits a different type of behavior from the other catalysts at high pressure. During the first three hours a very rapid deactivation occurs. After this time the deactivation rate is similar to that observed during the low pressure carbon deposition run. The turnover number data in Table 2 and the larger amount of carbon for Ni-Mo-Cu relative to Ni (Table 3) suggest that the rate of gasification of the deposited carbon is slower at high pressure resulting in more C_β formation and more rapid deactivation. The presence of Cu probably inhibits the gasification step by limiting the area available for H_2 to adsorb and since higher CO partial pressure increases the rate of C_α formation, a net increase in C_β occurs. Ponec (12) showed that for CO adsorption on Ni-Cu/SiO$_2$ powder the surface Ni concentration increased with time. Assuming such a change in Ni-Mo-Cu, the increasing concentration of Ni on the surface would increase the rate of gasification with the net effect of slowing down the rate of C_β formation, thus accounting for the lower deactivation rate observed after three hours.

Effects of Pre-sulfiding. Separate gravimetric studies in this laboratory (4,5) have shown that pre-sulfiding the catalyst substantially reduces the gasification rate without significantly affecting the rate of inactive carbon deposition. The result is increased C_β formation (4,5) and more rapid deactivation of pre-sulfided Ni-Mo-Cu and Ni relative to the fresh catalysts (see Table 3).

Carbon Deposition in a Fluidized Bed. As might be expected Ni-Mo-Cu and Ni-Mo deactivated more rapidly in a fluidized bed than in a fixed bed due to more uniform exposure to the reaction mixture. However, Ni-Mo-Cu deactivated more rapidly than Ni-Mo, a result opposite to that obtained in the fixed bed. Perhaps this can be accounted for by the lower space velocities and lower conversions associated with the fluidized bed reactor. The rate of carbon formation is proportional to the partial pressure of CO. The lower conversion would translate to a higher CO partial pressure at the catalyst surface which would affect each catalyst differently because of their different compositions. Careful examination of the low pressure fixed bed data of Tables 2 and 3 reveals that Ni-Mo and Ni-Mo-Cu suffered approximately the same percentage loss of surface area, but that Ni-Mo contained ten times more carbon after the steady-state carbon deposition run. Thus under the higher CO partial pressure Ni-Mo-Cu might be expected to deactivate more rapidly than Ni-Mo since increased carbon deposition would have more effect on Ni-Mo-Cu. A possible additional effect is that under uniform exposure to the reactant mixture a greater modification of the surface occurred for Ni-Mo-Cu than for Ni-Mo. Since large concentration and temperature gradients are absent in the fluidized bed, these results are much more indicative of the true deactivation behavior. Moreover, they model better the behavior anticipated in the BI-GAS process.

Regeneration of Carbon Fouled Catalysts in Air/Oxygen

The restoration of activity following regeneration provides strong evidence that carbon fouled catalysts can be regenerated with dilute mixtures of air or oxygen. In fact, this may be the only practical approach since in industrial equipment the regeneration temperature is usually limited to 700 K, and significant carbon gasification by steam, H_2 or CO_2 does not occur at temperatures below 800 K (16,17). The increase in CH_4 turnover number for the catalysts after the high pressure dilute O_2 treatment was more than could be accounted for by simple removal of the deposited carbon. This could be the result of a surface modification by the O_2 treatment and/or a modification which occurred during reaction as discussed previously.
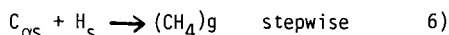
Palmer and Vroom (18) showed that the activity of nickel is increased by high temperature treatment with O_2 as a result of incorporating dissolved O_2 just below the surface. Sexton and Somorjai (15) reported similar results. Unfortunately this effect appears to be only temporary, since the specific activity of regenerated Ni/Al_2O_3 returned to the same value as the fresh catalyst after 24 hours of reaction at 623 K H_2/CO = 4, a condition chosen to ensure that further deactivation did not occur.

Regeneration of methane activity by oxygen is not without a price, however. The results show an overall decrease in surface area after carbon deposition and regeneration of 18 to 71%. This surface area loss is undoubtedly a consequence of sintering and even loss of the catalyst crystallites themselves. Rostrup-Nielsen (19) reports that deposited carbon grows in long hollow filaments with the Ni crystallite at the end. Transmission electron microscopy studies in this laboratory (20) confirm this observation. The Ni crystallite is thus removed from the support by the carbon filament and when the carbon is removed by oxidation the crystallite is probably carried out of the reactor with the gas stream. In fact, chemical analysis of fresh and regenerated Ni/Al_2O_3 samples revealed a 7% loss of nickel. It may be, therefore, impractical to regenerate carbon-fouled catalysts with air or oxygen since after a few cycles of deactivation and regeneration a large part

of the active surface of the catalyst would be gone. It depends, of course, on how much Ni is removed per treatment and the frequency of treatments.

A Model for Deactivation by Carbon

We propose a model to account for deactivation of nickel by β-carbon in a fixed bed during methanation. The proposed model for deactivation is a modification of that proposed by Wise et al. (21) for interaction of sulfur with Ni. A modification in the reaction mechanism is also made to account for the transformation of C_α to C_β and the loss of activity for surface reaction between C and H as the number of available nickel sites diminishes. Our proposed model is

$$CO_s \longrightarrow C_{\alpha s} + O_s \qquad\qquad\qquad 5)$$

$$C_{\alpha s} + H_s \longrightarrow (CH_4)g \qquad stepwise \qquad 6)$$

$$2C_{\alpha s} \longrightarrow C_{2\beta s} \qquad\qquad\qquad 7)$$

where the subscript "s" denotes an adsorbed species. Since the α state represents single carbon atoms which are easily gasified and the β state represents poly-atomic carbon which is much less active it is reasonable to assume that the dimerization of single C_α atoms to C_β causes the deactivation observed for Ni and Ni bimetallic methanation catalysts.

According to our proposed model the rate of deactivation due to carbon fouling is proportional to the rate of C_β formation which is proportional to the net rate of C_α formation. The rate of C_α formation is in turn proportional to the partial pressure of CO and the activity of the catalyst. Assuming first order dependence on both of these variables, an expression for the deactivation rate can be written as $da/dt = -k_d[CO]a$ where k_d = deactivation rate constant, $[CO]$ = concentration of CO, a = normalized activity at time t. The deactivation model proposed by Wise et al. for sulfur poisoning (21) can be adapted by assuming the reaction rate to be first order in CO concentration and that there are no radial concentration gradients. Simultaneous solution of the deactivation rate expression and the equation of continuity in the z direction (direction of flow) yields Equation 1. The following expression also results if z/V<<1, where V is the velocity in the z direction.

$$\ln\left[\left(\frac{1}{1-x_{CO}}\right)-1\right] = \ln[\exp(ka_oz/V)-1]-k_d[CO^o]t \qquad\qquad 8)$$

By plotting $\ln\left[\left(\frac{1}{1-x_{CO}}\right)-1\right]$ versus time t, values for k and k_d can be determined from the intercept and slope respectively.

Equation 1 is plotted as a solid line in Figure 2 using these parameters. It fits the data very well for the low pressure fixed bed runs. A similar development assuming no concentration gradient in the z direction leads to the exponential relationshp of Equation 3 for fluidized beds. Using Equations 1 and 3 we estimate that half of the active sites for Ni-Mo would be fouled in 37 days in a fixed bed and only 30 hours in a fluidized bed based on process conditions of $H_2/CO = 1.4$ and a space velocity of 3000 h^{-1}.

The fact that the proposed model for deactivation by carbon deposition predicts experimental behavior quite well indicates that it is consistent with the observed deactivation behavior -- i.e., the rate of deactivation increases as the partial pressure of CO is increased and decreases as the surface of the

catalyst is fouled by increasing accumulations of inactive carbon.

CONCLUSIONS

1. At 723 K and atmospheric pressure deactivation of nickel catalysts by carbon exhibited first order dependence on CO concentration (second order overall). Half-lives of Ni and Ni-Mo catalysts varied from 13-170 hours. Based on the specific intrinsic activities (CH_4 turnover numbers) after reaction under carbon depositing conditions the order of decreasing resistance to carbon deposition at low pressure was: Ni, Ni (pre-sulfided), Ni-Mo-Cu, Ni-Mo, Ni-Mo-Cu (pre-sulfided).

2. During reaction in a fixed bed at high temperatures and pressures little apparent deactivation was observed except in the case of Ni-Mo-Cu. The effects of deactivation were masked by the fast rate of reaction occurring in a portion of the bed. Thus the turnover numbers determined under reaction limited conditions reveal the true effects of deactivation.

3. Ni-Mo is more resistant to carbon deposition in a fluidized bed than Ni-Mo-Cu. The fluidized bed experiments provide more realistic indication of the true deactivation behavior because temperature and reactant concentrations are more uniform than in a fixed bed.

4. Pre-sulfiding the catalysts does not improve their tolerance to carbon deposition. In fact, pre-sulfiding Ni-Mo-Cu severely degraded its performance under severe carbon deposition conditions. It is believed that sulfur poisons the gasification of active carbon leading to a build up and transformation to inactive carbon.

5. A low pressure dilute air mixture at 573 K regenerates most carbon fouled catalysts. Using a dilute O_2 mixture at high pressure results in CH_4 turnover numbers and CH_4 yields which are temporarily higher than for fresh catalysts. Regeneration using air or O_2 results in a significant loss of surface area, but it may be the only practical method due to temperature limitations of industrial equipment.

ACKNOWLEDGEMENTS

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TABLE 1

CATALYST COMPOSITIONS AND SUPPLIERS

Catalyst	Metal Composition (wt.%)			Bulk Density (g/cm^3)	Support[b]	Supplier
	Ni	Mo	Cu			
Ni	14			0.54	γ-Al$_2$O$_3$[c]	BYU Catalysis Lab
Ni-Mo	10.9	19.8		0.91	Al$_2$O$_3$-SiO$_2$[d]	Climax Moly. Corp.
Ni-Mo-Cu	10	9[a]	3	0.86	Al$_2$O$_3$	Harshaw Chem. Co.

a) wt.% MoO$_3$

b) Powder form

c) Kaiser SAS Medium; 0.32 cm spheres

d) Harshaw AL-1605P (91% Al$_2$O$_3$, 6% SiO$_2$)

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TABLE 2

RESULTS OF DIFFERENTIAL REACTOR TESTS (498 K and 138 kPa)

Catalyst	Low Pressure Carbon Deposition[a]				High Pressure Carbon Deposition[b]			
	H_2 Uptake (μmol/g)	N_{CH_4}[c] (s^{-1})x10^3	Yield (%)[d] CH$_4$	CO$_2$	H_2 Uptake (μmol/g)	N_{CH_4} (s^{-1})x10^3	Yield (%) CH$_4$	CO$_2$
Ni								
Pre-Carbon Deposition	163	2.4	69	0	163	1.5	52	14
Post Carbon Deposition	142	2.6	43	0	--	0.8	31	1
Post Regeneration	135	2.1	68	0	147	2.7	86	14
Post Regeneration + 20 h at 623 K	--	--	--	--	148	2.7[a]	86[a]	--
Ni (Pre-Sulfided)								
Pre-Carbon Deposition	89	2.0	66	19	--	--	--	--
Post Carbon Deposition	--	1.9	42	0	--	--	--	--
Post Regeneration	99	2.4	85	0	--	--	--	--
Ni-Mo								
Pre-Carbon Deposition	83	2.8	53	3	83	0.35	29	20
Post Carbon Deposition	51	0.16	13	26	--	0.04	6.5	71
Post Regeneration	24	2.5	23	21	22	2.6	40	42
Post Regeneration FBR	41	2.2	43	9	--	--	--	--

TABLE 2 - Continued

Ni-Mo-Cu

Pre-Carbon Deposition	52	0.11	28	31	52	0.11	21	69
Post Carbon Deposition	37	0.15	27	46	46	0.01	8.5	73
Post Regeneration	30	0.11	21	30	---	0.31	32	34
Post Regeneration FBR[f]	25	---[e]	---[e]	---[e]	---	---	---	---

Ni-Mo-Cu (Pre-Sulfided)

Pre-Carbon Deposition	20	0.22	25	15[e]	---	---	---	---
Post Carbon Deposition	---	---[e]	---[e]	---[e]	---	---	---	---
Post Regeneration	18	---[e]	---[e]	---[e]	---	---	---	---

a) Conditions: 498 K, 138 kPa, 1% CO, $H_2/CO = 4$.

b) Conditions: 498 K, 138 kPa, 4.3% CO, $H_2/CO = 1.3$.

c) N_{CH_4} (turnover number) is the number of molecules produced per site per second.

d) Yield is percent CO converted which goes to CH_4/CO_2.

e) Too low to measure accurately.

f) FBR: Fluidized Bed Reactor run.

TABLE 3

RESULTS OF STEADY STATE (24 h) CARBON DEPOSITION TESTS (723 K, 138 or 2600 kPa, 100,000 h^{-1})

Catalyst	% CO Conversion		Initial CH_4 rate ($\mu mol/cm^3$ cat. s)	Normalized Activity after 24 h [a]	Half life [b] (h)	Carbon Content after 24 h (wt%)
	Initial	Final				
LOW PRESSURE						
Fixed Bed						
Ni	41	43	14	1.05	170	0.6
Ni (P)	33	34	11	0.93	134	--
Ni-Mo	43	31	9.0	0.67	50	16.8
Ni-Mo-Cu	33	27	9.6	0.81	107	1.7
Ni-Mo-Cu (P)	13	2	3.6	0.10	13	--
Fluidized Bed						
Ni-Mo	61	23	7.7	0.38	33	7.2
Ni-Mo-Cu	32	0	4.6	0	2[c]	0.6
HIGH PRESSURE						
Ni	94	91	36	0.99	--	--
Ni-Mo	81	83	21	1.05	--	--
Ni-Mo-Cu	81	52	25	0.63	--	--

a) Normalized activity = rate of CH_4 production divided by initial CH_4 production rate.

b) Half life = time at which normalized activity equals 0.5.

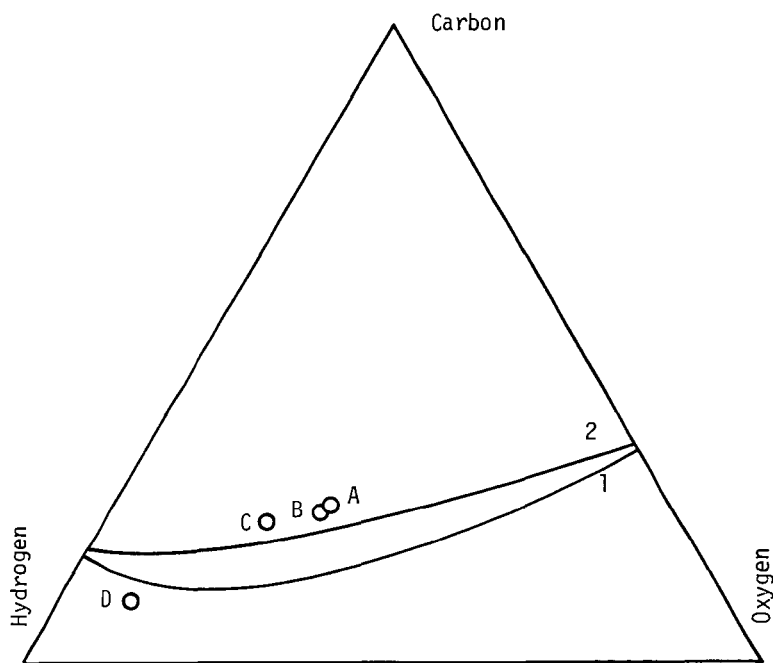c) No activity after 15 h.

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Figure 1. Equilibrium Diagram at 723 K and 138 kPa Showing BI-GAS and Test Feed Gas Compositions. A = BI-GAS, B = Fluidized Bed Runs, C = High and Low Pressure Runs plus some Differential Runs, D = Differential Runs. Curve 1 is the equilibrium curve based on graphite. Curve 2 is based on "non-ideal" carbon as reported by J.R. Rostrup-Nielsen in J. Cat. 27, 343-356 (1972).
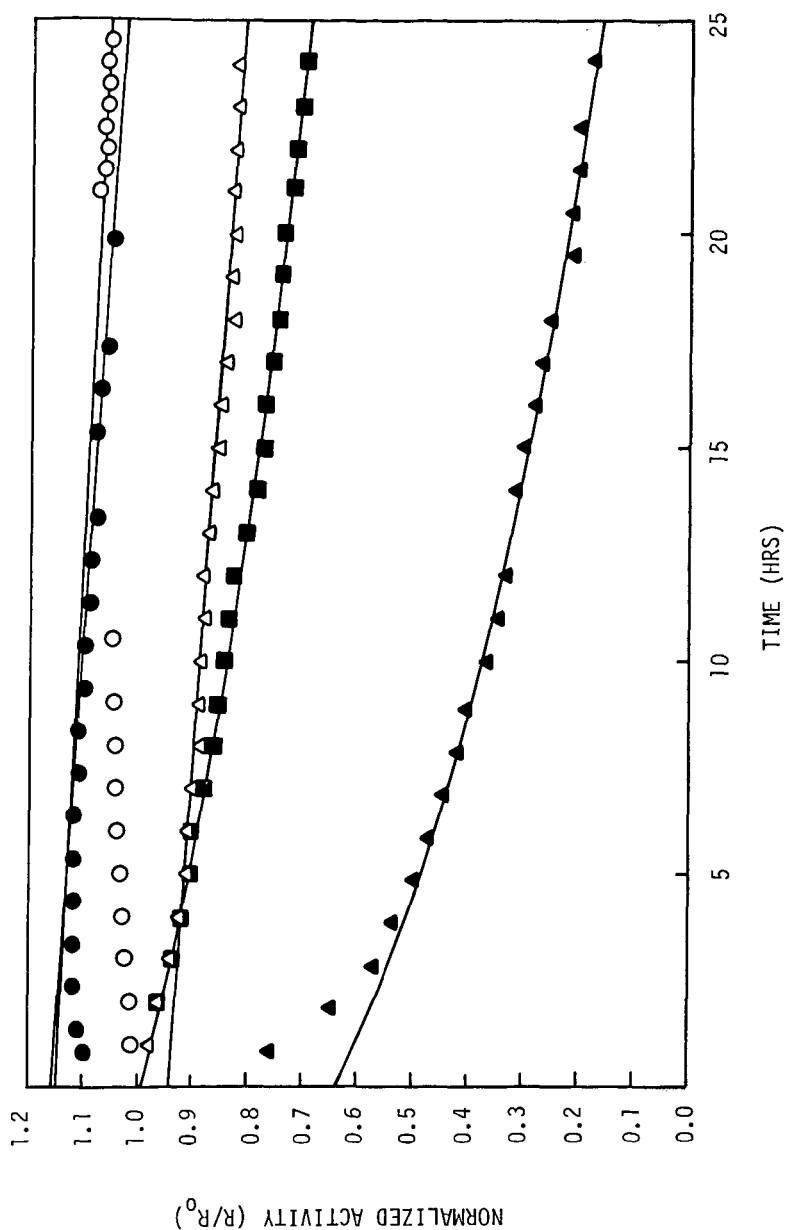
Figure 2. Variation of Normalized Activity with Time at Low Pressure: $\bigcirc$ = Ni, Pre-sulfided), $\triangle$ = Ni-Mo-Cu, $\blacktriangle$ = Ni-Mo-Cu (Pre-sulfided), $\blacksquare$ = Ni-Mo. Solid lines represent correlation of data by expression:

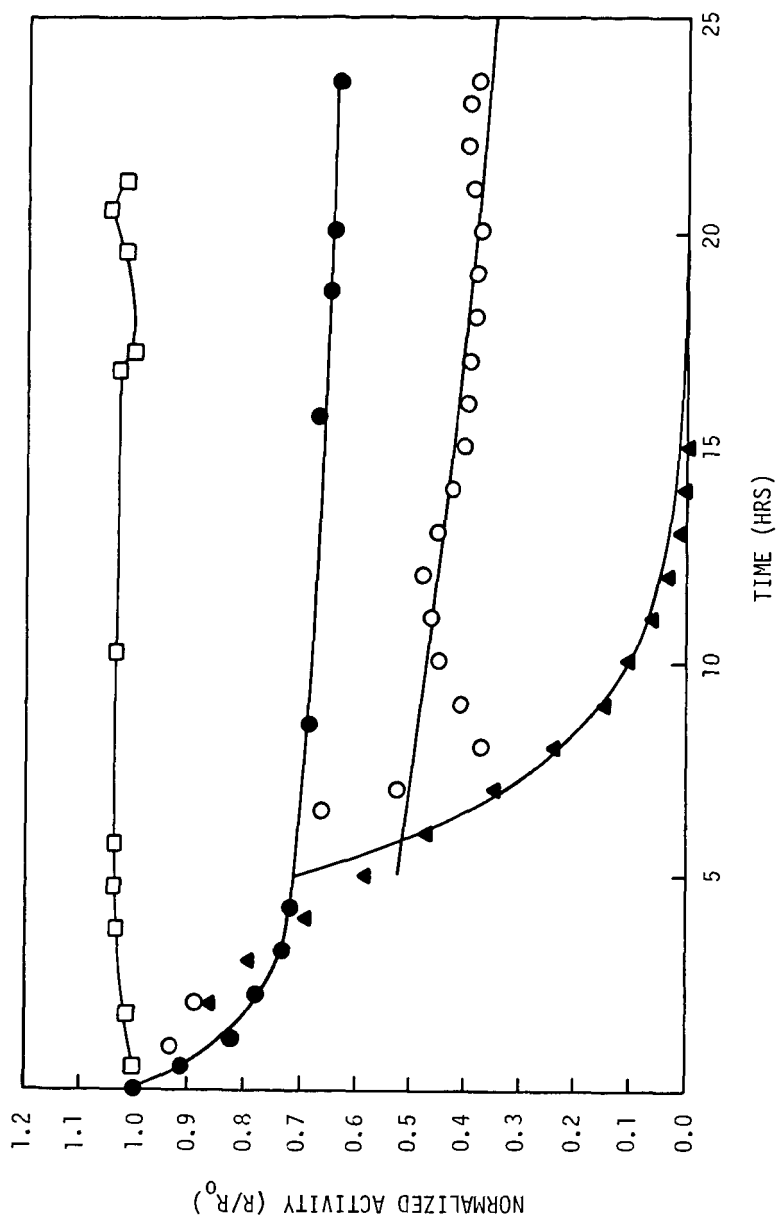$$a = \frac{a_0}{1+\exp(-ka_0\tau)[\exp(k_d[CO^\circ]t)-1]}$$

Figure 3. Variation of Normalized Activity with Time: $\square$ = Ni-Mo high pressure run, $\bigcirc$ = Ni-Mo low pressure fluidized bed run, $\bullet$ = Ni-Mo-Cu high pressure run, $\blacktriangle$ = Ni-Mo-Cu low pressure fluidized bed run. Fluidized bed data after 5 hours are correlated by the expression $a = a_o \exp(-k_d t)$.